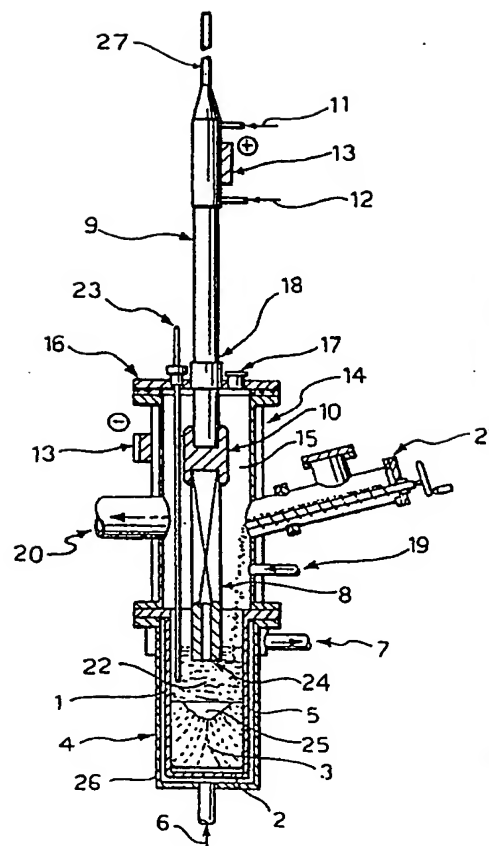# PCT

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(54) Title: PROCESS FOR THE ELECTROLYTIC PRODUCTION OF METALS

(57) Abstract

Process for the electrolytic production of metals particularly titanium and alloys starting from the corresponding compounds, by means of an apparatus for the electrochemical extraction including: a cathode–crucible (1) containing a mass of solidified metal (3), a liquid electrolyte (22) with a density which is lower than that of the metal and a pool of liquid metal (25) produced; one or more non–consumable anodes (8) partially immersed in the electrolyte with means for regulating their distance from the cathodic surface; a feeding system (21) to the electrolyte of the compounds of the metals, of the electrolyte constituents and of alloying materials; a power supply which feeds direct current to the liquid metal, and through the electrolyte, to the anodes, and causes the cathodic reduction of the metal in liquid form and the evolution of anodic gas, with the heat generation which maintains the electrolyte in the molten state; an air–tight containment structure in which the anodic gases generated during the electrolysis are collected.

PROCESS FOR THE ELECTROLYTIC PRODUCTION OF METALS

1) PREAMBLE

In order to improve an industrial electrolytic process we

5   need to take decisions which involve changes in physical
operating conditions.

We need therefore, to reach a practical understanding of
the physical meaning of the data which describe the
operative conditions of the process.

10   The first reason for the technological lag in the
development of the electrolytic process for producing Ti,
is the insufficient theoretical understanding of the Ti
system.

The second reason is that we cannot draw information from

15   the knowledge of the electrolytic process for producing
Al, since its theoretical formulation is far from a common
acceptance.

This state of the matter is the consequence of the
insufficient fundamental electrochemistry work; the

20   formalisms used in the published literature on the subject
are often devoid of a rational base and of a physical
significance.

In fact, when the metallurgists attempts to interpret the
phenomena occurring at a working single electrode, and

25   this is exactly what he is interested in, he gets

entangled in matters of principles about the thermodynamic
of electrically charged species.

This state of the science is especially pitiful when we
remember how much the electrochemistry has contributed to
5   the development of thermodynamics.

By reading the published literature, we can see that the
electrochemists still have fear to enter deep into the
matter, that is to abandon the reversible equilibrium
conditions, in which the metallurgists have no interest,
10   and to abandon the two-dimensional interface unrealistic
model.

The work which is illustrated herebelow, is an attempt
towards getting some understandable information of
practical usefulness about the processes occurring at a
15   single electrode, under steady state dynamic regimes, at
the microscopical level, away from reversible equilibrium
conditions. The resulting practical data are the object
of this invention.

The school of thought at the base of this work is
20   contained in the M.V. Ginatta Ph.D. Thesis (Ref. 1).

The descriptions which will follow are intended for
illustrating the characteristics of the Ti system within
the requirement of the patent application, therefore
without the use of rigorous irreversible thermodynamics
25   formalisms. The aim is, through a better understanding, to
achieve one of the object of this invention that is
improving the electrolytic process technology .

2) BACKGROUND OF THE INVENTION

Presently the electrolytic production of titanium is performed in molten chlorides systems and the metal produced has the form of pure crystals.

5   The industrial problem of chloride electrolysis is that titanium is deposited in the solid state on the cathodes, with crystalline morphologies of large surface areas and low bulk densities.

The growth of the solid cathodic deposit requires its
10 frequent removal from the electrolyte by means of handling apparata of the kind described in US Patent N. 4'670'121.

The titanium deposit stripped from the cathodes retains some of the electrolyte entrained among the crystals, and the subsequent operation of removing the
15 entrapped residual electrolyte, inevitably decreases the purity of the metal produced, which instead is very pure at the moment of its electrolytic reduction on the cathodes.

Also, the electrochemical characteristic of titanium
20 deposition onto solid cathodes limits the maximum current density at which the electrolysis can be operated, to relatively low values with correspondingly low specific plant productivity.

Further, in order to obtain crystalline deposits, the
25 concentration of titanium ions in the electrolyte must be in the range requiring a separation between the anolyte and the catholyte as described in US Patent N. 5'015'342.

The electrolytic production of titanium in the liquid state has several operating advantages with respect to the production of solid deposits, as for example:

- the cathodic area does not vary with the progress of the
5 electrolysis, thus the achievement and control of steady-state operating conditions is easier;

- the separation of the pure metal produced from the electrolyte is complete and does not require any further operation besides solidification and cooling under a
10 protecting atmosphere;

- the harvesting the metal produced can be performed without disturbing the progress of the electrolysis, as it will be explained in the description of the invention.

The electrolytic production of titanium at
15 temperatures around its melting point has a very important thermochemical advantage, since the titanium lower valence compounds have a very low regime concentration, within the electrolyte, at those temperatures; therefore, there are no disproportionation or redox reactions to affect the
20 current efficiency of the process (Fig. 9).

The electrolytic production of titanium at temperatures above its melting point has a very important electrochemical advantage, since the exchange current density values on liquid Ti cathodes are very much higher
25 than those on solid Ti cathodes.

Furthermore, the addition of a minor ionic compound to the main electrolyte component, further increases the values

of the exchange current density, since does not allow the
formation of ionic metal complexes which are responsible
for slowing the cathodic interphase processes.

5   3)   BRIEF STATEMENT OF THE INVENTION

The matter of the invention is defined by the claims which
follow.

One of the object of the present invention is the
electrolytic reduction of titanium metal in the liquid
10   state.

An object of this invention is the use of the thermal
blanketing provided by the electrolyte, in order to
maintain a large pool of liquid titanium which grants the
operation of full liquid cathodes. This mode of operating
15   permits the use of much higher current densities with
respect to solid cathodes.

Another object of this invention is the complete
separation of titanium from the electrolyte in the
cathodic interphase during the electrochemical reduction
20   at high current densities.

Another object of this invention is the accurate control
of the electrochemical half reactions occurring at the
cathode, by means of the monitoring system which also
actuates the variations of the process electrochemical
25   parameters.

Another object of this invention is the use of a further
advantage of the electrolysis with liquid cathodes,
consisting in the possibility of operating the reduction
of the metal from a low concentration of titanium ions in
5   the electrolyte, while maintaining high current densities,
and achieving high current efficiencies.

For titanium electrochemical systems, a specific
electrolyte is not available, that is, equivalent to what
cryolite is for aluminum, which could allow the feed of
10   titanium oxides to the cell and obtaining titanium metal
with a oxygen content within current trade specifications.

However titanium has the advantage of a large worldwide
production of titanium tetrachloride of high purity which
is mostly dedicated to the pigment industry.

15   Since titanium mineral concentrates must, in all cases, be
purified of impurities we may as well use the well
established carbochlorination process to purify titanium
raw material, just as the aluminum industry use the Bayer
alumina refining process.

20   What could be further advantageous in order to reduce the
cost of titanium electrolytic production would be the
commercial establishment of a second type of titanium
tetrachloride of a lower purity, and of a lower cost, with
respect to the grade used for pigments.

25   This for two order of considerations:

- the inherent refining capability of molten salt electrolytes which can maintain in solution some of the impurities or can separate others as vapor;

5　　- some of the elements which are regarded as impurities by the pigment industry, are actually alloying metals for titanium alloys (for example: V, Zr, Al, Nb)

It is understood that this second brand of titanium tetrachloride could only be obtained by the producers when the volume of the production of electrolytic titanium will

10　be larger.

Another object of this invention is a method for dissolving titanium tetrachloride in the electrolyte. Since $TiCl_4$ has a very small solubility in molten salts, but the reaction kinetics of TiCl4 with calcium is very

15　fast, the operating conditions that this invention teaches, are such that a concentration of elemental calcium be present in the electrolyte.

Calcium is coreduced at the cathode when titanium ion concentration is maintained at low values and, being

20　almost insoluble in titanium, elemental calcium diffuses in the body of the electrolyte towards the volume in which TiCl4 is being fed.

Another object of this invention is the method for feeding titanium raw materials to the electrolyte.

25　One of the possible embodiments in which TiCl4 is fed is through the passageway in the body of the insoluble anode, carried by a tubing, preferably made of a chemically inert

material and not electrically conductive, such as BN and
the like, so as to separate the volume in which TiCl4
reacts with calcium, from the anodic interphase in which
chlorine gas is evolved.

5   As another embodiment object of this invention, chlorine
gas coming out of the electrolyte goes up into the space
between the electrode side and the cell enclosure inner
wall. The wall of the cell structure is preferably cooled
to enhance the solidification of the vaporized bath
10   constituents onto the inner wall, to obtain a protection
for the structure metal from the attack of chlorine gas.

Another object of this invention is a method to minimize
the dismutation reaction

$(3Ti^{2+} = 2Ti^{3+} + Ti°)$ and to benefit from its effects.

15   The low titanium concentration of the electrolyte, taught
by this invention, favors the establishment and the
maintenance of the equilibrium. The circulation movements
of the electrolyte under operating conditions bring
elemental titanium near the cathodic interphase where it
20   coalesces into the liquid metal.

Conversely, some of the titanium ions that are carried
near the anodic interphase are oxidized to tetrachloride,
which is very effective for eliminating the current
density limit constituted by the anode effect.

25   Furthermore elemental titanium present near the feeding
point of titanium tetrachloride reacts with it to give
lower valence titanium ions.

Another object of this invention is the method by which
the absolute amounts of all of these reactions are
minimized by the presence of the taught concentration of
elemental calcium dissolved in the electrolyte, which
5   reacts very effectively and maintains the steady-state
operating conditions.

Another object of this invention is a method for assisting
the prereduction of TiCl4 by using an electronically
conductive means for feeding the compound, connected with
10   the negative terminal of a separate power supply, or to
the apparatus power supply through a current control mean,
in analogy with the teaching of US Patent N. 5'015'342.

This operating mode is taught for ensuring a complete
absorption of TiCl4 by the electrolyte at high rates of
15   titanium production, but it is not always required.

Another object of this invention is a method for
monitoring the temperature of the electrolyte, and gives
readings which are not disturbed by the apparatus
currents.

20   A temperature probe is conveniently installed within the
tubing which carries the titanium raw material feed within
the anode body.

The temperature at that location is representative of the
resistance heat produced by the electrolysis current, and
25   the temperature reading is accurate.

Instead on the outside of the anode the cooling effect of
the cooled structural wall produces solid electrolyte
crust which hinders the temperature measurement.

Another object of this invention is a method for
5   controlling the temperature of the electrolyte in order to
maintain the steady-state operating conditions with a
cathode liquid metal pool of a optimum depth.

Another object of this invention is a method for
maintaining a steady-state production of electrolytic
10   titanium.

In the operating conditions, taught by the invention,
TiCl4 is a gas, but at ambient temperature it is a liquid
which is very conveniently handled by a metering pump. By
entering the passageway within the working anode TiCl4 is
15   vaporized, and further heated passing in the feed tubing.

Under the described conditions the rate of TiCl4
absorption by the electrolyte is very fast and its
efficiency is almost unity.

The set of operating conditions object of this invention,
20   makes very easy the regulation of controls for the rate of
feeding of TiCl4, in order to be proportional to the
direct current supplied to the apparatus.

Another object of this invention is a method for using
graphite as an insoluble anode materials in molten
25   fluorides.

The selection of TiCl4 as the raw material as thought by
this invention makes carbon electrodes behaving as

insoluble, therefore minimizing the tendency of producing
fluo-chloro-carbon compounds, which are unstable anyway at
the temperature of the operations, which are within the
range used for the thermal decomposition of these

5   compounds into the incinerators.

Another object of this invention is the geometrical
configuration of the anode, in particular of its part
immersed in the electrolyte.

We have found that for maintaining an even current

10   distribution through the electrolyte the anode is
preferably shaped as an inverted cone. Also the presence
of radial groves enhance the evolution of anodic gas
bubbles.

Another object of this invention relates to the methods

15   for harvesting the metal produced.

The simpler method is that in which the liquid metal pool
within a cooled crucible, gradually solidifies and becomes
an ingot which grows in height with the progress of the
electrolysis.

20   In the apparatus object of the invention the anode is
insoluble and thus does not change its length during the
metal production; therefore a means for raising the anode
in order to maintain constant all the electrochemical
parameters is provided.

25   The end of the raise is reached when the ingot has grown
up to fill the crucible; at that point the electrolysis is

interrupted to allow the harvesting of the ingot produced,
and then restarted for the continuation of the process.

A more elaborated way of harvesting the metal produced is
similar to that used in the continuous casting of metals,
5   in which the growing ingot is gradually removed through a
bottomless crucible.

In the apparatus object of this invention a level control
system raises and lowers the insoluble anode within the
interval required to follow the ingot growth and downward
10   movement, in order to maintain constant the operating
parameters of the electrolysis. .

A method for harvesting of metal produced still in the
liquid state is taught in the US Pat N. 5'160'532 by Mark
G. Benz and regards the cold finger orifice controlled by
15   induction melting.

It is another object of this invention the retrofitting of
the cell with the cold finger induction orifice control
system as a preferred configuration for the tapping of the
liquid titanium produced.

20   This is a discontinuous operation that must be
synchronized with the anode level control, but it is
essentially continuous for large cathodic areas cells.

Another object of this invention is the direct production
of titanium alloys by using the apparatus as described.

25   The alloying elements are introduced in the electrolyte
both together with the TiCl4 feed making use of their

solubilities, and added through a solid feed port as
metals, as master alloys, as compounds.

The required chemical composition of the produced alloys
is a function of the electrochemical characteristics of
5   the alloying metals, and thus times and amounts fed are
set to achieve the target specifications for the produced
alloys.

Another object of this invention is the high homogeneity
of the alloys produced, as compared to the traditional
10 melting technologies. This is due to the low rate of
metal transfer, as compared to the rate of transfer in
ingot melting, that, coupled with the electromagnetic
stirring of the liquid metal pool, caused by the passage
of the electric current, results in the production of very
15 homogeneous metallic alloys.

Another object of this invention is the direct production
of metal plates of large surface area, that permits the
saving of the costs of metallurgical work for transforming
cylindrical ingots into blooms and slabs and than into
20 plates, especially for difficult to mill alloys.

Another object of this invention is the direct production
of metal billets intended for the metallurgical
transformation in long metal and alloy products, which
saves expensive metallurgical work and metal scrap
25 generated during the processing of large cylindrical
ingots.

4) BRIEF DESCRIPTION OF THE DRAWINGS

The process and apparatus object of the invention will be described in greater details by means of working
5   examples which will follow, and with reference to the appended drawings wherein:

- figure 1 is a partially-sectioned front view of an apparatus for carrying out the process according to the invention;

10   - figure 2 is a partially-sectioned front view of an apparatus for carrying out the process according to the embodiment of example 1;

- figure 3 is a partially-sectioned front view of an apparatus for carrying out the process according to the
15   embodiment of example 2;

- figure 4 is a vertical-sectional view of a crucible for carrying out the process according to the embodiment of example 3;

- figure 5 is a cross-sectional view of a crucible for
20   carrying out the process according to the embodiment of example 4;

- figure 6 is a section taken along the line IV-IV of figure 5;

-       figure 7 is a vertical sectional view of an apparatus
for carrying out the process according to the embodiment
of example 5;

-       figure 8 is a vertical sectional view of the anodes-
5   cathodes area of an apparatus for carrying out the process
according to the embodiment of example 6;

-       figure 9 is an equilibrium diagram of the variation
of the concentration of the titanium species with
temperature;

10 -   figure 10 is a schematic drawing of the microscopic
model for the cathodic interphase under dynamic steady-
state operating conditions.

DEFINITIONS

1)   The **Cathodic Interphase** is a three-dimensional
15 medium (not a two-dimensional interface), that is, a
volume in which the electrode half-reactions occur; it is
located between the electronically conductive cathode and
the ionically conductive electrolyte.

Within the thickness of the cathodic interphase there are
20 steep gradients in the concentration of the ions and of
the atoms, and in all physico-chemical variables. For
example, the electrical conductivity value goes from the
electronic mode at 10'000 ohm-1 cm-1 in the bulk of the
metallic electrode, to the ionic mode at 1 ohm-1 cm-1 in
25 the bulk of the electrolyte. Inside the interphase the
energy density has very high values, that is the notions
of solid, liquid and gas are not applicable.

For details see page. 163 of Ref.1.

2)   All the cathodic and anodic processes are driven by
the DC power supply (which is external to the cell, but
part of the electrochemical system) which applies an
5   electric field (difference in potential energy of
electrons) between an electronically conductive cathode
and an electronically conductive anode.

3)   Under common operating conditions of Ti cells, the
difference in decomposition potentials between Ti compound
10   and K compound is small, that is,

it can be stated that the process of Ti reduction is only
slightly thermodynamically more noble than the process of
K reduction.

4)   The ionic diameter of Ti+ is about 1.92 A°; it can be
15   stated that the process of reduction to Ti° is not
kinetically privileged with respect to the K° reduction.

5)   The role of ionic current carrier in the electrolyte
is almost totally done by

K+:   t+=0.99.

20

5) BASIS OF THE INVENTION

The process objects of this invention provides conditions
for the reduction of titanium multivalent species to
titanium metal.

The attached schematic drawings (Fig. 10) summarizes the microscopic mechanism which is believed to occur within the thickness of the cathodic interphase in the electrolytic production of liquid Ti, according to the

5   electrodynamic model proposed by M.V. Ginatta, Ph.D. thesis, Colorado School of Mines (Ref.1).

The definitions of the terms used in the description of this invention are reported in Section n. 4.

The microscopic mechanism represents the real dynamic

10   steady-state operating conditions in which there are chemical reactions and electrochemical reactions, occurring simultaneously, but at a different locations, driven by the gradient of the electrochemical potentials, that is the local chemical potential of the species,

15   induced by the externally applied electric field.

To facilitate illustrating the process object of this invention, the description will begin with the electrolytic cell start up operations and will progress towards the steady-state regime conditions, with the

20   assumption that the cathodic interphase is a multilayer.

The system comprises an electrolyte constituted by CaF2, KF, KCl and elemental K, Ca, a liquid Ti metal pool as the cathode, and a TiCl4 injection means.

The DC power supplied by the rectifier, at a low voltage

25   and low cathodic current density, causes the reduction of K° on the liquid Ti metal pool cathode, in which K has very little solubility, with simultaneous Cl2 evolution at the non-consumable anode.

With the progress of the electrolysis, the concentration of K° in layer Q increases, with respect to the low concentration of K° in layer B.

At the start up, the layers R and S are thought as not

5   being present yet.

This mode of operation generates a chemical potential difference between Q and B, which drives K° away from Q into B.

The K° enters B, where it reacts with the $TiCl_4$ which is

10   being started to be injected, to produce K_3TiF_6, which is a stable complex of Ti^{3+}, and KCl which is a stable chloride.

For Coulomb interaction, the triple charged, small, Ti^{3+} ion, can go to bind $6F^-$ at a very small interionic

15   distance, thus with great bonding energy.

Ti^{3+} is a small ion since it has lost 3 electrons, over a total of 22, and thus, being the positive charge of the nucleus unchanged, the remaining 19 electrons, having to share the same total positive charge, are attracted much

20   closer to the nucleus.

In fact Ti° atomic diam. is 2.93 A°, while Ti^{3+} ionic diam. is 1.52 A°, which is 1/7 in volume.

Thus, at low current density (e.g. < 1. A/cm^2) the cathodic system is composed of only the B layer, in which

25   K_3TiF_6 is formed, and the Q layer in which K° is reduced.

By increasing the voltage, thus the current density, with
the production of more K°, the layer R is created, and the
destabilization of K3TiF6 is induced with the formation of
TiF6(3-) and 3K+ which creates the layer S.

5   The complex TiF6(3-) cannot enter R, much less Q, because
its overall charge is very negative.

The K° arriving from R, approaches the complex TiF6(3-) in
S and use F- for transferring 1 electron to Ti3+, which
expands to Ti++ (ionic diam. 1.88 A°, that is double in
10 volume) and thus releases the F- .

This reaction generates as a product Ti++, which is a
double charged ion, that has an average dimension, it is
not complexed by F-, and it is driven towards the cathode
by the ionic electric field, much in the same way as the
15 other cations.

Thus Ti++ entering R along with K+, encounters K°, which
has a higher chemical potential, coming from Q, and thus
it reduces Ti++ to Ti+. In fact in R the chemical
potential of K is greater than in S, but not high enough
20 for producing Ti°.

Now Ti+ is a single charged ion, with dimensions
comparable to K+; it is driven by the ionic electric
field to enter Q along with K+ and it is co-reduced to Ti°
together with K°, by the electrons available in Q.

25 Ti° coalesces into the liquid Ti pool, and K° having very
low solubility in Ti, accumulates on top of the Ti pool.

Therefore, at medium current densities (e.g. > 1. A/cm2)
there is the establishment of the layer S in which K3TiF6
is decomposed and Ti++ formed, and of the layer R in which
Ti++ is further reduced by K° to Ti+.

5   The cyclic voltammetric analysis confirms in part the
above microscopic mechanism for the start up conditions;
in fact, coming from anodic and going towards cathodic
potentials at 0.1 V/sec, there is a series of peaks that
can be assumed to represent a series of steps at which
10   partial reduction/oxidation reactions occur.

However, cyclic voltammetric results give only limited
information since they are measurements of unsteady-state
transient conditions.

Besides, some of this step partial reactions have
15   extremely fast kinetics, and the exchange current
densities of these cathodic systems have very high values.

By further increasing the voltage of the power supply, we
increase the electrical potential difference between the
pool of Ti and the layers boundary Q/ R, with the effect
20   of supplying more electrons to Q (higher cathodic current
density) to reduce more K+ and Ti+, with the final result
of producing more K° and more Ti metal.

The chemical potential of K° in Q becomes much higher that
of K° in R, and thus in S, with the effect that more K°
25   is driven out of R into S, to react with more TiF6(3-),
and to reduce more Ti++; which then enters R to be reduced
to Ti+ by more coming K°.

Also the physical thickness of the Q, R and S layers
increases with the applied greater current density values,
along with the increase of the chemical potential of K°
in R and in Q.

5   Continuing with the multilayer assumption for the purpose
of facilitating the illustration of the object of the
invention, the higher cathodic potential differences
applied by the power supply and the resulting increasing
cathodic current densities, produce a thickening of the
10   cathodic interphase, with the establishment of a well
characterized series of layers, within each of them, a
specific step of the multistep reduction reaction takes
place.

The multilayer structure of the cathodic interphase is
15   dynamically maintained by the applied power of the DC
rectifier.

In each of the layers constituting the cathodic
interphase, there are different values of electrochemical
potentials for the species involved. This dynamic steady
20   regime allows the stepwise reduction of multivalent ions,
one electron at a time, in well defined different layers.
These are the loci of the discrete discontinuities that
are the main characteristic of the electrochemical
systems.

25   For steady-state regime operating conditions, we can
summarize which reactions is concurrently occurring where,
according to the microscopic mechanism, as follows:

- in B: TiCl4 + K° + 6KF   =   K3TiF6 + 4KCl , both stable
products;

- in S: K3TiF6 + K°   =   4KF + TiF2 ,   both unstable
ionized products;

5   - in R: K° + Ti++ + 2F-   =   K+ + 2F- + Ti+ ;

- in Q: 3K+ + 3é = 3K°   and   Ti+ + é =
Ti° .

Now, by considering this proposed microscopic mechanism in
more detail, we can see the possibility of electron
10   transfer through a bipolar mechanism of K°, that is, the
exchange of electrons between K° (atom) and the adjacent
K+(ion), thus transferring the electric charge, in the
direction of the electrolyte, without physical mass
transfer.

15   This consideration may explain why there is no measurable
cathodic overvoltage in this type of cell, even at high
current density values.

With some analogy with the process of electrolytic metal
refining processes with bipolar electrodes, we may go
20   further and think that, under steady-state operating
conditions, it may be no need for more net reduction of
further K°, since its chemical potential gradient from Q
to S is being maintained by the electron transfer and
countercurrent Ti+ migration.

25   The understanding of the importance of the role in which
K°/K+ are engaged in this type of cells, may also explain:

- why the K content of the Ti produced, is below the
equilibrium data, and

- why the current efficiency increases with increasing the
current density, and

5   - why, after the power supply has been shut off, the back
e.m.f. remains for minutes, producing a depolarization
curve of a particular shape; that is, at first, the layer
Q may be thought as to work as a discharging battery '
negative electrode, consuming $K° = K+ é$; than, the
10   resulting decrease of chemical potential of $K°$ in Q,
drives $K°$ from R and from S into Q, that is making the
interphase work as fuel cell anode, until there is $K°$ in
B.

However, the start up mechanism of the electrolysis is not
15   exactly the reverse of the depolarization phenomenon.

On solid cathodes, only the very initial starting
conditions can be represented by the microscopic
mechanism, since, soon after, the crystallization
generates discontinuities on the metal surface which
20   destroy the uniformity in current density distribution.
The microscopic mechanism can only occur at the tip of the
growing dendrites, while the roots at the starting
cathodic surface are not electrochemically working any
more.

25   Some of the embodiments illustrated in the present
invention are based on establishing the above mechanism
for the electrolysis.

However, other embodiments of this invention are based on
the following considerations.

The large scale operations of the chloride process as
taught by US Patent N. 5015342, always showed that the
5   anolyte contained in the composite electrode (TA)
comprising the bipolar titanium electrode (TEB), was free
of Ti ionic species (at all times it was pure white NaCl).
The Ti lower valence ions that seeped through the TEB,
were completely precipitated as Ti crystals by elemental
10   Na which was present on the frontal side of TEB. This was
confirmed by the absence of TiCl4 in the Cl2 anodic gas
evolution under regime steady state operations.

The TiCl4 was detected in the anodic gases only when the
Ti crystals accumulated in large quantities at the TA
15   bottom, as a result of a malfunction of the TEB. The Ti
crystals accumulation wrapped the graphite anodes and
started being chlorinated by the nascent Cl2.

Thermodynamic equilibria analysis made in the 1980's
confirmed that, in the presence of alkali metals and
20   alkaline earth metals, the reduction of TiCl4 to Ti
crystal, at 1100°K, is complete with near zero equilibrium
concentration of Ti lower chlorides in the electrolyte.

The consequent solution of the above chloride process
problem, was the continuous removal of the Ti crystal
25   produced within the TA, which, however, involved
elaborated engineering plant design [attention: this
matter has not been patented].

However, further thermodynamic equilibria analysis showed
that the above operating conditions exist up to 2200°K,
both for chlorides and fluorides, and at this temperatures
all Ti present is liquid, with near zero concentration of

5   Ti lower valence ions (Fig. 9).

These are some the reasons why the electrolytic process
taught by this invention produces Ti in the liquid state
and does not require diaphragms.

Further thermodynamic analysis showed the beneficial

10   effects on the process taught by this invention, obtained
by the combined action of monovalent alkali metals and
divalent alkaline earth metals present in the electrolyte,
as for example, Ca° + K°, Ca° + Na°, or any other
combination like Ca° + Mg°.

15   These operating conditions, not allowing stable metal
complexes to form, result in firther increases of exchange
current density values, and thus of allowed process
current density.

Operating at high temperature is further beneficial

20   because the differences in the decomposition potential at
2100°K between the alkali metals and alkali earth metals
fluorides, and Titanium fluorides, are much less than the
differences at 1100°K .

In fact, the negative temperature coefficient value for

25   Titanium fluorides (0.63) is much smaller than those for
the alkali metals and alkaline earth metals fluorides
(1.06); this means that with increasing temperatures, KF

26

decomposition potential dicreases more rapidly than that
of TiF2.

Lastly, the most appropriate concentrations of the
species, for codeposition, are determined by activity
5   coefficient calculations.

Concluding, the melting point of Ti, 1943°K, being within
the temperature interval indicated above, permits the
operation with liquid cathodes, with all the
electrochemical and operative benefits mentioned above.

10 From the results of the microscopic mechanism and of the
thermodynamic analysis, it became very evident the need
for engineering efforts to invent electrolytic cells which
operate within the window of conditions indicated above.

That is, one of the object of this invention is the
15 electrolytic cells that make use of the very fast
kinetics, and the very high exchange current densities of
molten salts electrolytes, which work best at high current
density regimes producing liquid metals.

The presence of minor constituents in the electrolyte,
20 that is chlorides additions, increase the ionic electrical
conductivity of the electrolyte; therefore, for a
constant joule heat formation rate, a thicker electrolyte
can be used than in pure CaF2, that is a larger distance
between cathode and anode can be maintained for the same
25 applied voltage.

This mode of operation is beneficial for limiting the back reaction of Cl2 recombination with desolved Ca° in the electrolyte.

5

6) DETAILED DESCRIPTION OF THE INVENTION

The process object of this invention comprises the simultaneous occurrence of chemical reactions in the bulk 10 of the electrolyte, and of electrochemical reactions in the anodic and cathodic interphases.

To help the illustration of the invention, the method and the apparatus according to the present invention are described in details by means of the following embodiments 15 of working examples.

Example 1

The apparatus described in the following example allows the electrowinning of titanium and titanium alloys from its compounds, particularly fluorides, chlorides, 20 bromides and iodides, through electrolysis in a molten salt electrolyte kept at a temperature higher than the melting point of titanium and its alloys.

The apparatus vertical view of figure 1, is semischematically illustrated in figure 2, and comprises 25 of a cathode 1, consisting preferably of a copper

cylinder, which is closed at its lower end 2 to allow the
crystallization of a titanium ingot 3.

The internal diameter of the copper cylinder is e.g.
165 mm, height 400 mm, wall thickness 12 mm.

5   The cathode-crucible 1 is housed in a vessel 4 which
is closed at its lower end and is greater in size than the
copper crucible so as to define an hollow space 5, which
constitutes a water jacket for the circulation of cooling
water.

10   Water, or another cooling fluid, is fed to the jacket
through water inlet 6 at a temperature of about 15°C and
exited through water outlet 7 at a temperature of about 30
°C, with a velocity of 3 m/sec.

With 8 is indicated an anode, which is a cylindrical
15 electrode, coaxial and concentric with the crucible, made
of graphite, having a diameter of 80 to 120 mm. The anode
tip being preferably in the shape of an inverted cone for
better current distribution through the electrolyte, and
it has radial grooves to enhance chlorine gas evolution.

20   The anode is connected to a water-cooled bus bar 9,
by means of a nickel plated copper clamp 10.   Inlet and
outlet for the cooling water are indicated respectively
with reference numerals 11 and 12. The bus bar 9 is
connected to the positive terminal of a power supply 13.

25   The cathode-crucible is connected and air-tight
sealed to a cover 14, made of stainless steel, which
defines an inner chamber 15, to avoid the transfer of

oxygen from the atmosphere to the ingot. The cover is provided with a lid 16 having an observation port 17, and the bus bar 9 is inserted into the lid by means of a vacuum-tight gland 18. The process can however also be carried out in plants without a closing cover making use of the protection offered by the crust of solidified electrolyte.

A protective argon atmosphere can be introduced into the chamber 15 through inlet 19 and then vented through outlet 20.

The cover 14, that is in electrical contact with the cathode-crucible walls, is connected to the negative terminal of the power supply 13 to allow the coaxial current feeding.

The apparatus is provided with a feeder-conveyor 21 which is integral with the cover to introduce solid electrolytes and the alloying elements under controlled atmosphere conditions. Molten salt electrolyte contained in the crucible is indicated as 22.

The electrolyte consists preferably of mixture of CaF_2 (99.9% pure) and calcium (99% pure) in grains of 3 - 6 mm in size to permit a regular start up procedure, and it is kept liquid at the desired temperature of about 1750°C by the energy dissipated by Joule effect of the current passing through the electrolyte. The weight ratio in the Ca/CaF_2 electrolyte is, for instance, 1:10; in addition, other salts may be added to the electrolyte in order to optimize the anodic and cathodic reactions.

In order to obtain the production of metals of the highest purity, an ESR melting of the electrolyte is a preferred procedure for purifying the CaF_2. It is performed in a water-cooled Mo-Ti-Zr alloy crucible with a

5   titanium electrode at a temperature below the melting point for Ti, in order to fuse only CaF_2 (m.p. 1'420°C) and eliminate its contaminants.

The amount of salt introduced into the crucible is such to provide for a electrolyte height of about 25 to 75

10   mm, and the level at which the graphite electrode 8 is immersed in the molten salts is determined considering that CaF_2 has a specific electrical resistivity of 0.20 - 0.25 ohm cm at 1'900 - 1'650 °C.

A potential difference of 5 to 40 V for example, is

15   applied between anode and cathode by feeding a direct current which can be adjusted between about 3'000 and 15'000 Amp.

At the start, and whenever it may be needed, an alternating current is applied to ensure the reaching of

20   the desired temperature in the molten electrolyte.

The process may also be carried out with combined heating systems, by providing an additional heat source (e.g. plasma torches, induction heating, resistance heating and the like) to supply a portion of the energy

25   required to keep the salt bath at the preferred temperature range between 1'700 and 1'900 °C.

The compounds containing the metal to be extracted (e.g. $TiCl_4$, TiF_3, $TiBr_4$, TiI_4, TiC, in the case of

titanium production) are fed both in the liquid and solid state by means of a feeder 21. TiCl4 and other compounds which can be fed in the liquid and gaseous state are preferably fed to the electrolyte through the tubing 23.
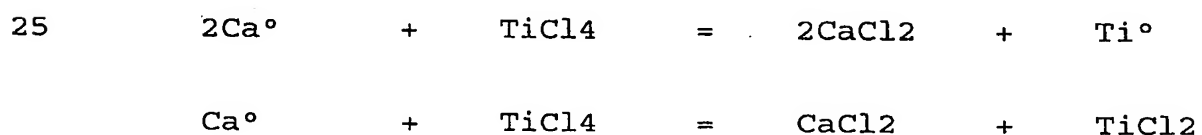
5   The quantity of the alloying materials added are determined taking into account their partial equilibrium thermodynamic values in the process conditions; for example AlCl3 and VCl4 (which could be VOCl3 if crude TiCl4 is used) are fed in the embodiment of this
10   invention for the production of ASTM Gr 5 titanium alloy.

In a preferred embodiment the alloying elements which forms chlorides which are soluble in TiCl4, are admixed with it and fed together into the electrolyte through the duct 23.
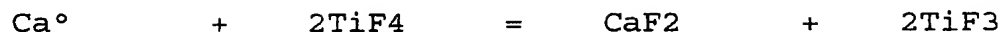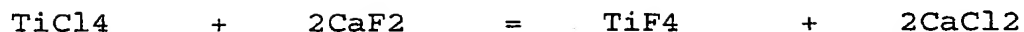
15   The feeding cycle for alloying materials which are fed in the solid state are within 10-30 minute periods depending on the solubility limits for the alloying materials in the electrolyte at the operating conditions, and are preferably fed with the feeder 21.

20   The gaseous products generated by the electrolysis, such as Cl2, F2, Br2, I2, CO/CO2 are removed preferentially by a coaxial duct 24 inside the anode 8.
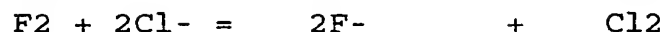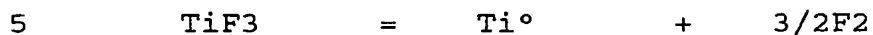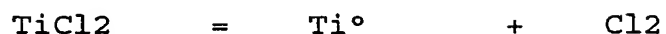
The following reactions are believed to take place inside the electrolyte:

25     $2Ca° + TiCl4 = 2CaCl2 + Ti°$

$Ca° + TiCl4 = CaCl2 + TiCl2$

$$TiCl4 \quad + \quad 2CaF2 \quad = \quad TiF4 \quad + \quad 2CaCl2$$

$$Ca° \quad + \quad 2TiF4 \quad = \quad CaF2 \quad + \quad 2TiF3$$

and at the electrodes:

$$TiCl2 \quad = \quad Ti° \quad + \quad Cl2$$

5
$$TiF3 \quad = \quad Ti° \quad + \quad 3/2F2$$

$$F2 + 2Cl- = \quad 2F- \quad + \quad Cl2$$

$$CaCl2 \quad = \quad Ca° \quad + \quad Cl2$$

The above reactions only summarize the final result of the chemical and electrochemical mechanisms which occur
10 in the cell, and products which are obtained. Similar reactions are believed to involve the alloying elements and compounds in the embodiment of this invention for producing metal alloys.

Calcium metal, released by its chloride, diffuses in
15 the electrolyte and it is available for the reduction of titanium tetrachloride. Alternatively, calcium chloride may be added to the electrolyte instead of elemental calcium.

Titanium obtained at the electrolyte temperature is
20 collected in the liquid state into the cathode, by forming a liquid metal pool 25 and it is allowed to solidify therein.

The copper crucible is protected against the fluoride ions corrosive attack, by a layer of slag 26 which

solidifies in contact with the cooled walls. The thickness of that layer is kept at about 1-3 mm.

In the course of the process, under steady state conditions, the metal ingot 3 that forms inside the
5   crucible grows vertically in height.

The apparatus object of this invention is provided by a process control system to regulate the vertical movement of the cathode-electrolyte-anode assembly, by means of an anode drive system 27 to ensure constant metal production
10   conditions.

The control of the electrolytic production is preferably actuated by means of a current regulator that guaranties the continuous raising of the anode in order to maintain constant current supply conditions.

15   During the process, the control system adjusts the anode immersion depth in the electrolyte, following the advancing of the metal pool surface, in order that the current be kept constant at the set value.

This mode of operation can be summarized as follows,

20

$$L = \frac{V_e \ S_a}{I \ r_e}$$

where:

L   =   distance between anodic surfaces and cathodic
surfaces;

V_e =   voltage drop through the electrolyte;

5   S_a =   anode surface area;

I   =   current supplied;

r_e =   specific resistivity of the electrolyte.

Only as an example, which is not meant to be
restrictive, the values of cathodic current densities used
10   are in the range from 1 A/cm2 to 60 A/cm2, with the
preferred interval being between 10 and 50 A/cm2.

The values of current densities used in the apparata
object of this invention, are higher than that for
aluminum production, since for the case of titanium
15   reduction for example, the metal fog phenomenon is less
important. In fact, the difference in density between the
liquid metal and the electrolyte, at their respective
electrolysis operating conditions, is of only 0.25 g/cm3
for aluminum, while is about 1.80 g/cm3 for titanium.

20   This is also a reason why in the embodiments of this
invention we can make use of calcium reduction of titanium
ions in the bulk of the electrolyte and consequent
coalescence of droplets into the liquid cathode.

Particularly, the cathodic interphase is a highly
25   reductive environment for titanium ions which are directly

reduced by electrons or through the help of calcium reduction oxidation mechanism. In fact, at the operating conditions of the electrolysis, calcium is codeposited with titanium on the liquid cathode surface, but having a very low solubility in titanium, calcium returns into the electrolyte.

In addition, the passage of the process current generates a vigorous electromagnetic stirring of the liquid metal pool which further enhances the mass transfer at the cathodic interphase.

Also the electrolytic gas evolution at the anodes produces a further acceleration of mass transfer rates which allow the use of high current densities.

Since CaF_2 has a very low electronic conductivity and a very high ionic conductivity, the electric charge transfer mechanism through the electrolyte is entirely ionic.

To better illustrate the physical significance of mass transfer it is important to stress that the process object of this invention is an electrowinning of metals from their compounds dissolved in the electrolyte.

This process is the most comprehensive among all the metallurgical processes since it starts from the raw material, that is a compound in which the metal is contained in an oxidized ionic form, and, in only one apparatus it arrives to the production of the metal in the reduced, elemental, pure form.

Therefore the mass transport entirely occurs by means of the ionic current which goes through the electrolyte between the anode, that remains geometrically unchanged since it is not soluble under the electrolysis conditions,

5   and the liquid cathode, using the energy for winning the decomposition potential of the metal compound dissolved in the electrolyte, and for liberating the metal and the anodic gas separately.

This electrowinning process is operationally much

10   more complex and energetically more intensive with respect to the simple electrolytic refining process, in which the anode is made of an impure metal to be purified, that is already in its elemental reduced form.

A further simplified and accelerated mass transfer

15   process is the electroslag melting in which the purification of the metal is minimal, being essentially the physical collapse by fusion of the upper electrode, the anode, because the temperature reached by the slag, as a result of the current passage, has overcome the melting

20   point of the metal constituting the upper electrode. In this case the mass transfer is almost entirely elemental, by means of the fall of the metal in form of drops through the slag, and the contribution of the ionic mass transfer by the electrolytic refining process is minimal.

25   Instead, in the apparatus object of this invention, the positive electrode, the anode, not only is insoluble in the electrolyte but has a very high melting point, that cannot be reached by the temperatures of the operating conditions, thus allowing only the ionic electrochemical

mass transfer mechanism to occur for the electrowinning of
the metal from the electrolyte.

Example 2

5   The apparatus described in the following example
differs from that of example 1 in the cathode-crucible
geometrical configuration which is made to obtain long
slabs and ingots with some analogy with the metal
continuous casting procedure.

       The main process parameters are similar and, in
10   figure 3 the same reference numerals are used to indicate
the same or similar components.

       The cathode consists of a rectangular water-cooled
copper mold 1 with its lower end closed by a retractable
water-cooled base plate 28 provided with a water inlet 29
15   and outlet 30, to allow the extraction of a titanium ingot
3.

       The base plate 28 is electrically connected to the
negative terminal of the power supply 13, and it is water-
cooled through inlet 29 and outlet 30.

20   The mold dimensions are for example as follows:

- cross-section area: 200 cm3

- side-to-side ratio: 2-4

- height: 1.5 x internal longest side.

The anode 8 is rectangular and the ratio of the cross-sectional areas of the anode and ingot is in the range from 0.3 to 0.7 .

5   The anode is made of graphite, the immersed part of which may be coated with a refractory material.

With the progress of the electrolysis, under steady state conditions, the amount of metal that forms in the mold increases. Since the mold is fixed, the base plate shall be made to move downwards by drive means that

10   withdraw the ingot at a rate synchronous with the metal reduction rate.

The downward movement of the base plate 28, following the growth of the titanium ingot 3, is controlled by a electronic system which maintains constant the vertical

15   location of the liquid cathode surface, of the pool 25, within the copper cylinder. In this way also the vertical position of the anode 8 is maintained constant to insure a constant electrolyte thickness.

The apparatus allows to obtain ingots over 3 meters

20   long, thanks to the retractable base plate. The outcoming ingot is already solidified but still at high temperature and in the case of a reactive metal (e.g. titanium and titanium alloys), it is preferably protected from the external atmosphere by a lower cover 14b.

25   The compounds containing the metals to be produced are preferably fed through the passageway 24 within the anode 8, in which a tube 8b, preferably made of a chemically inert and electrically non conductive, is

inserted in order to separate the volume in which TiCl4 is reduced, from the anodic interphase in which anodic gases evolve.

The geometry of the inert tube 8b is such that it can slide inside the passageway 24, so to retract in order not to interfere with start up operations, and to slide down to a set position when the electrolyte is molten.

The gaseous byproducts are exited preferably through the outlet 20.

The feeder 21 is used preferably for additions of solid metal compounds, of electrolyte components, and alloying elements and compounds when alloy ingots are produced.

This example refers to an apparatus using a retractable base plate system, but the same results can be obtained by using a mold that is movable with all its ancillary equipment and a fixed base plate. A combination of both systems is also possible.

The apparatus described in this example permits to obtain ingots with excellent surface finish, which can be sent to the mill plant without any further metallurgical operation.

Example 3

The apparatus described in the following example differs from that of example 1 in the cathode-crucible configuration which is made to obtain a withdrawal in the liquid state of the metal produced.

As illustrated in figure 4 the apparatus comprises of a cathode-crucible 1, consisting preferably of a copper cylinder, which is closed at its lower end by means of a cold hearth 41, provided with a radially segmented crucible 44 and a cold finger orifice 47, to allow the withdrawal of the liquid metal stream 40.

The volume of the liquid metal pool 25 is controlled by the intensity of cooling through water inlet 42 and outlet 43, counterbalanced by the intensity of heating provided by the induction coils 45 and power supply 46 to the segmented crucible 44.

The cold hearth 41 is electrically connected with the negative terminal of the power supply 13 in order to operate the electrolytic process for the cathodic reduction of the metal and its alloys.

The withdrawal of the liquid metal accumulated in the pool 25 is preferably discontinuous and a process control system, as described in example 1, is provided in order to regulate the electrolyte-anode vertical movement by means of a electrode drive assembly 27.

To activate the withdrawal of liquid metal, the electrical power to the induction coils of the cold finger orifice 47 is gradually increased in order to obtain a stream of molten metal into a lower container 48, which is air-tight sealed with the cold hearth 41, and maintained under controlled atmosphere for assuring the purity of the metal produced.

The withdrawal of liquid metal can be continuous, particularly for large cathodic surface apparata.

Example 4

5   The apparatus described in the following example differs from that of example 2 in that the cathode-crucible geometrical configuration is designed to produce flat thin slabs, while the main process parameters and functioning features are similar.

10   The cathode-mold 1, shown in the cross-sectional view of figure 5, consists of two water-cooled copper plates 31, and 32, that are 600 to 1'300 mm wide, and are joined by lateral water-cooled copper spacers 33, and 34, that are 100 to 15 mm thick. These dimensions are not meant to

15   restrict the applicability of the invention, but are only given as an example.

The tightness of the assembly for the containment of the liquid metal is ensured by the electrolyte layer that solidifies in the junctions between water-cooled copper

20   members.

A plurality of graphite anodes 35 are inserted and lined up along the long side of the cathode-crucible.

A plurality of metal compounds feeders 36 are installed in such a way that each of them has its lower

25   end immersed in the electrolyte between the anodes 35.

In analogy with the apparatus of example 2, the crucible is provided with a retractable water-cooled base plate 37, illustrated in figure 6, which allows the gradual withdrawal of the produced metal slab, from the
5   bottom of the mold, to a length suitable for the metallurgical rolling operations.

The amount of current and the electrolyte thickness are electronically regulated for optimum temperature equalization by a control equipment.

10   Example 5

The apparatus described in the following example differs from those of examples 1 and 2 in the cathode-crucible geometrical configuration made to obtain wide flat plates, slabs and ingots, while the main process
15   parameters and functioning features are similar.

As illustrated in figure 7 the cathode consists of a rectangular water-cooled copper mold 1 with its lower end closed by a water-cooled copper plate 2.

The internal dimensions of the copper mold are for
20   exemple 1'000 mm width and 2'000 mm length. The height is between 500 and 1'000 mm to permit the production of a titanium flat plate 250 mm thick for example.

In this embodiment of the invention, the structure comprising the mold 1, the housing vessel 4, the cover 14,
25   a plurality of anodes 8, the anode drive assembly 27, are resting on the base plate 2 during operation of the electrolysis.

This structural assembly, in a preferred embodiment, is lifted at the end of the process to allow the harvesting of the titanium plate 3, and the bus bars connecting the positive terminal 13 of the power supply are flexible.

The anodes 8 have a geometrical configuration which is similar to those used in one type of chlorine producing electrolytic cells, and preferably have a plurality of passageways for the withdrawal of the anodic gases.

Between the anodes and preferably within the body of the anodes are the ducts 24 through which the compounds of the metals to be extracted are fed.

The anode drive assembly 27 permit the adjusting of their vertical position in order to maintain constant the electrolyte thickness, following the growth of the titanium plate during the electrolysis. A current of 200 kA will results in a production of a plate of about 1.8 ton of titanium per day for example.

The atmosphere within the inner chamber 15 is controlled by means of the vacuum tight gland 18 and of the gasket within the grove at the lower end of the mold 1.

Example 6

The apparatus described in the following example differs from those of examples 4 and 5 in the cathode-crucible and anodes geometrical configuration made to

obtain billets, while the main process parameters and functioning features are similar.

As illustrated in figure 8 the cathode-crucible consists of a series of water-cooled copper partitions 32,
5   joint by lateral water-cooled copper spacers 33, which forms a number of rectangular elongated molds, that rest on a water-cooled copper plate 37.

The height of the partitions and the width of the spacers are designed for producing billets of 140 x 140 mm
10   cross section , more than 3 meters long for example.

Another difference with respect to the previous example 5 is the independent height control mechanism for each row of anodes, to ensure an even cathodic reduction of the metal in all compartments.

15   Since this is a preferred embodiment for the production of billets of metal alloys that go to the manufacture of long products, the additions of alloying material is performed in the liquid-gaseous state through ducts 24, and in the solid state by means of feeders 36,
20   21, as indicated in the previous examples.

Example 7

The apparatus described in the following example differs from those of examples 1 to 6 in the electrolyte composition, which is made to use the beneficial effects
25   of the combined presence of monovalent alkali metals with divalent alkaline earth metals.

The apparatus and the main process parameters are similar and apply to all figures from 1 to 8.

One of the possible electrolyte compositions consist preferably of CaF_2 with for example 9% KF, and amounts of $CaCl_2$ and KCl, and $Ca°$ and $K°$, which depend on the feed rate of $TiCl_4$ relative to the total current; 3%$Ca°$ and 3%$K°$ for example.

The lower electrical resistivity of the electrolyte compositions taught in this example, permits the operations of the cell with a thicker bath, at higher current densities, while keeping the system at the desired temperature.

With this mode of operation, near 100% yield for $TiCl_4$ reduction reaction is obtained, together with very high cell productivity. KCl and $CaCl_2$ allows the continuation of Cl_2 gas anodic evolution for the case of $TiCl_4$ injection discontinuities.

CLAIMS

What we claim is:

1.   Process for the electrolytic production of metals
5   and alloys starting from their corresponding compounds,
which uses an electrowinning apparatus comprising:

-       a cathode-crucible containing a solid metal skull, a
liquid electrolyte having a density that is lower than the
metal, and a liquid pool of the metal produced;

10 -   one or more non-consumable anode partially immersed
in the electrolyte with means for adjusting their distance
from the cathodic surface;

-       a means for feeding metal compounds, electrolyte
constituents and alloying materials to the electrolyte;

15 -   a power supply means for supplying direct current to
the metal pool, and through the electrolyte, to the
anodes, causing the cathodic reduction of the metal in the
liquid state, and the anodic evolution of anodic gas, with
the generation of heat that maintains the electrolyte
20 molten;

-       a air-tight vessel in which anodic gases generated
during the electrolysis are conveyed.

2.   The process of claim 1 wherein the metals that are produced are titanium, zirconium, thorium, vanadium, chromium, nickel, cobalt, yttrium, beryllium, silicon, rare earths and mishmetal.

5   3.   The process of claim 1 wherein the alloys that are produced are formed by metals selected from the groups called reactives, refractories, of transition, lanthanides and actinides.

4.   The process of claim 1 for the production of
10   titanium, wherein the electrolyte is a mixture of calcium fluoride, calcium chloride and calcium metal.

5.   The process of claim 1 or 4 wherein the electrolyte comprises alkali metals and alkaline earth metals compounds.

15   6.   The process of claim 1 or 4 wherein the metal compounds which are fed to the electrowinning apparatus are fluorides, chlorides, bromides and iodides.

7.   The process of claim 1 wherein the cathode-crucible is a copper crucible.

20   8.   The process of claim 1 wherein the crucible is cooled thereby causing the solidification of a protecting layer of the electrolyte on the inside surfaces.

9.   The process of claim 1 wherein the air-tight vessel is cooled to produce the condensation of the vapors coming
25   from the electrolyte, onto its internal surfaces, thereby protecting the vessel from the attach of the anodic gases.

10. The process of claim 1 wherein the anodic gases, generated during the process of metals electrowinning, are conveyed through ducts made inside the non-consumable anodes.

11. The process of claim 1 wherein the compounds of the metals being produced are fed into the electrolyte through ducts made inside the non-consumable anodes.

12. The process of claim 1 wherein the feeding of the compounds of the metal being produced is performed by means of a tubing of an electrical insulating and chemically inert material, in order to separate the volume in which said compounds are reduced, from the anodic interphase in which the anodic gases are evolved.

13. The process of claim 1 wherein the production of alloys is obtained by feeding the apparatus with elements and compounds in quantity proportional to their electrochemical characteristics in order to achieve the specified chemical composition.

14. The process of claim 1 wherein the electrowinning apparatus comprises means for the continuous withdrawal of the solidified metal produced.

15. The process of claim 1 wherein the metal produced in the liquid state is withdrawn by means of a cold finger induction orifice.

16. The process of claim 1 applied to the production of plates, slabs, blooms, billets of metals and alloys.

17. The process of claim 1 wherein the anode immersed in the electrolyte, has its lower end shaped and machined to enhance the anodic gases evolution.

18. The process of claim 1 wherein the current is fed by means of cooled anodic busbars.

19. The process of claim 1 wherein the apparatus comprises a vacuum-tight gland for the anodes drive mechanism.

20. The process of claim 1 comprising a computer system for monitoring the steady-state operating conditions, in order to maintain the steady-state by adjusting the distance between the anodes and the liquid cathodic surface.

21. The electrowinning apparatus having the characteristics enunciated in claim 1.

22. The process of claims 1 or 4 or 5 wherein the electrolyte comprises additions of monovalent alkali metals and divalent alkaline earth metals, as $Ca° + K°$ or $Ca° + Mg°$.

FIG. 1

FIG. 2
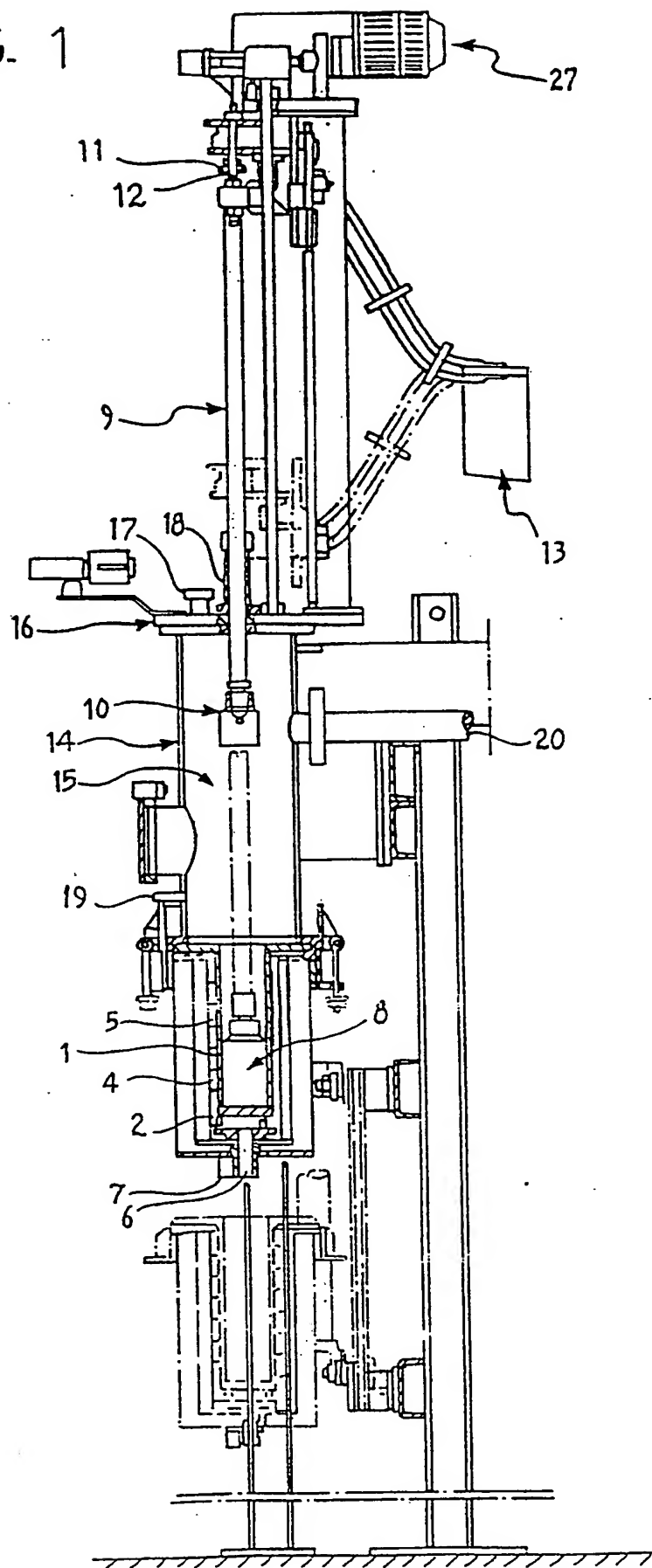
FIG. 3

FIG. 4

FIG. 5

FIG. 6

FIG. 7

FIG. 8

FIG. 9

FIG. 10